Presidential Green Chemistry Challenge Awards

Title: Process for Production of Chemicals and Carbon from Waste Tires, Plastics, Carpet and Biomasses

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New Process for Production of Chemicals and Carbon from Waste Tires, Plastics, Carpet and Biomasses

On June 27, 2011 a Provisional Patent Application (# 61/571,383, C. Rogers) was submitted to the US Patent Office that describes a new low temperature chemical process for the depolymerization-decomposition of plastics, carpet, tires, and other biomass materials to recover monomers, oligomers, or a usable carbon product.

The nominated technology described below is eligible for the Small Business Award. The technology focus area is the use of greener reaction conditions**.** All research and development effort has been done in the United States.

In the 1990`s, the original BCD technology (Patent # 5,019,175; 5,039,350; 5,064,526 C. Rogers, et al) is a chemical process which was invented by Charles Rogers, et al while employed by the USEPA Laboratory, Cincinnati, Ohio. This non-combustion toxic waste destruction technology is approved by the USEPA and Basel Convention countries. For over 18 years it has been used nationally and internationally. For information on BCD technology, please go to http://www.ihpa.info/docs/library/reports/Pops/June2009 or Google "application of BCD in Czech Republic". Since retiring and no longer associated with the USEPA, Charles and BCD Group-II, Inc. have continued working on developing recycling technology and discovered entirely new catalysts, base medium and reagents, and lower temperatures known as CTH technology.

Abstract:

On July 7, 2011 a patent application was submitted to the U.S. Patent Office (Provisional Application # 61/571,383) that describes a new low temperature chemical method (modified BCD process) or Catalytic Transfer hydrogenation (CTH) that converts plastics, tires, rubber, other polymers and biomass materials into chemicals or a solid product with carbon contents of 84% and higher. The complete analysis is carbon 84.70 %, hydrogen 6.86%, Sulfur 0.604% Zinc 1.3% and 6.54% other inorganic additives. Existing conventional pyrolysis processes lose over 1/3 carbon as gaseous products, require much higher processing temperatures, and produce vast amounts of greenhouse gases (carbon oxides). The CTH process produces no carbon oxide and there is little carbon loss as gaseous products resulting in products having a higher carbon content.

The CTH process chemistry is non-oxidative and operates at temperatures of 130 - 300° C. The CTH process, unlike pyrolysis and liquefaction processes that operates at much higher temperatures of 450–700° C, depolymerizes or converts polymeric materials into reusable chemicals and carbon at lower temperatures and within 30 - 90 minutes. The proprietary reaction medium is composed of an alkali metal carbonate or hydroxide, hydrocarbon donor–solvent, and a proprietary catalyst-water absorption agent. Reactive hydrogen released from the hydrogen donor at lower temperatures than the original BCD process affects cleavage of hetero atoms in processed materials to produce monomers, oligomers, polymer from copolymers and sodium salts of anions. Depolymerization of polyester, polyurethane, polycarbonates or carpets by existing technologies requires much high temperatures, pressures and expensive reagents.

Coal is one source of coke which is used as fuel in Solid Oxide Fuel Cells (SOFC). Coke production requires processing for 16 to 24 hours at temperatures of around 2000° C. Carbon produced from tires and biomass materials by the CTH process is usable as SOFC fuel. Also, studies have shown that this carbon product is easily converted into Syn gas. Laboratory scale studies to depolymerize and recover polypropylene from copolymers waste generated by the food packaging and auto industry were completed in 2011 with C-4 Polymer Inc., Chagrin Falls, Ohio. Pilot scale completion is scheduled for completion in early 2012 and commercial development to be initiated in late 2012. Licensees of the original BCD process and an India Chemical firm have expressed interest in this CTH technology. Also, this technology is to be presented to Venture Capitalists by the Environmental Business Cluster, Silicon Valley, California.

Nominated Technology Details

Globally, discarded tires are among the largest and most problematic source of waste. Numerous research efforts have been ongoing for many years to recycle tires, plastics, carpets and biomass feed stocks into cost-effective reusable products. Recently the USEPA reported that scrap tires contaminate the U.S.-Mexico Border region, posing a serious threat to the environment and public health. Along with being ideal breeding grounds for mosquitoes, rats and other disease vectors, tire piles are fire hazards that, if ablaze, can generate acute air, water and land contamination.

In 2006, the University of California completed a study for the State of California entitled "Technology Evaluation and Economic Analysis of Waste Tires Pyrolysis, Gasification, and Liquefaction". There were more than 34,000,000 tires annually for disposal in California. It was found in this study that a hypothetical plant that processed 5 million tires per year could produce gross revenue of over $13.2 million from the combined sales of such products as electricity, chemicals, and diesel fuels as well as residual carbon black. It is apparent that this study assumed the existence of cost-effective tire conversion technology.

Liberty Tire Company headquartered in Pittsburgh, PA is now a major provider of tire recycling services in the United States. Reportedly, Liberty Tire annually transforms more than 110 million tires into reusable raw materials and products. Much of the recycled rubber produced by Liberty Tire is used as crumb rubber, industrial feedstock, tire derived fuel, or rubber mulch for landscaping and playground applications.

US-Mexico Border Scrap Tires

Technologies are being developed and used to recycle tires, plastics, and biomass. However, there are still vast amounts of this waste that must be discarded annually in landfills.

Modified BCD: Catalytic Transfer Hydrogenation (CTH) Process

The process chemistry that affects depolymerization and carbon production from tires and polymeric materials is presented below:

$$\text{R-X} + \text{H*-Donor} + \text{NaOH} \xrightarrow[130\text{ -}300^\circ\text{ C}]{\text{Catalyst}} \text{R} + \text{H*-Donor} + \text{H*OH} + \text{NaOH} + \text{NaX} + \text{H2}$$

R-X is representative of hetero atomic compounds converted into a carbon residue (R). The hydrogen donor H*-Donor is usually a high boiling point aliphatic hydrocarbon. When under the influence of proprietary catalyst and base, reactive hydrogen is released from donor to cleave heteroatom bonds. The partially hydrogenated compound in the presence of the catalyst releases its hydrogen resulting in carbon formation. The resulting products are salts of anions, water, ammonia when nitrogen is present, and hydrogen. Commercial BCD processing plants are equipped with a chemical stirred reactor, chillers and condensers. Analysis of the non-condensable gases from plant condenser reveal the presence of hydrogen, C2 and C3 compounds in the gas stream. Commercial operating plants flare the gas to prevent release of these constituents into the environment. The lower temperatures are employed to produce chemicals and the higher process temperatures to produce carbon products. The carbon products have been analyzed by Galbraith Laboratories, Knoxville, TN and has been shown to contain 84% carbon content. The carbon product has been tested by Professor Steven S. Chuang, Akron University, Akron, Ohio and determined to be a useful fuel for Solid Oxide Fuel Cells (SOFC). Also, Professor Takahiro Yamada, University of Dayton Research Institute (UDRI) has determined that this carbon can be readily converted to Syn gas.

Applications of CTH for Plastics Recycling

A large number of polymers, copolymers and thermoplastic composites are depolymerized (DP) by existing processes to monomers and oligomers. However, many of the existing commercial DP processes shown in Table 1 require higher temperatures, pressures, and expensive catalysts or reagents to depolymerize polymers. The CTH process readily depolymerizes polyesters (PET), polyurethane (PU), polycarbonates (PC), nylons and other polymers into reusable products under mild conditions, rapidly and without use of expensive reagents. CTH affects the DP of polymers under non-pressurized conditions at low temperatures of 130-200° C. Most importantly, color sorting of most polymers is not required since dyes, foreign and toxic materials are extracted into the hydrocarbon phase of the system. The Figures 1, 2, 3, 4a and 4b reveal highly colored PET and nylons are depolymerized by the CTH process and with separation of color. Toxic agents and dyes present in the hydrocarbon phase are readily destroyed by the CTH process to a carbon residue as described in the November 11, 2011 issue of Chemical Engineering on page 15. The degree of DP is controlled by base concentration and

temperature. Monomers are produced when stoichiometric amounts of base are introduced into the medium. Oligomers are produced when non-stoichiometric base is employed.

Table 1. Comparison of CTH to Conventional DP Technologies

Solvent for depolymerization	Reaction Temperature (° C)	Reaction Pressure (MPa)	Reaction time	Catalyst	Recycled monomers	References
Supercritical methanol (MHI)	300	15	10 minutes	Not used	DMT/EG	MHI proprietary technology
Supercritical methanol (others)	300	6	30 minutes	Not used	DMT/EG	Reference 5
Supercritical methanol (MHI)	230	6,5	5 hours*	Not used	DMT/EG	MHI Proprietary technology
Liquid methanol	180	2,5	5+ hours	Used	DMT/EG	Reference 5
Ethylene glycol	190 to 200	3 to 4	5+ hours	Used	BHET	Reference 5
New CTH process (CTH)	130 to 200	None	20 – 30 minutes	Used	monomers oligomers polymers	Patent pending technology

Low cost chemicals make up the reaction medium which is recovered and reused for subsequent processing. The monomers, oligomers or polymers are recovered from the reaction medium after neutralization followed by filtration or centrifugation.

Polymeric Products Separated and/or Depolymerized by the CTH process

The following polymeric materials have been successfully processed by the CTH process in conjunction with C-4 Polymer Inc. for polymer recovery:

1. Nylon 6 and 6, 6 recovery from carpet
2. Polycarbonate laminated fabric (recovery of Bisphenol)
3. Thermoplastic composites, recovery of PET from copolymer composed of Polypropylene-PET-Carbon fiber
4. Polyurethane recoveries from laminated fabrics
5. HDPE recoveries from PET co-polymer
6. Nylons from polyethylene
7. PC from lens shaving residues
8. PET from PVC laminated fabric

Figure 1 – Shows a) PET prior to depolymerization, b) after DP and phase 1 separation with green dye c) dried PET product.

Figure 2 - Shows separation of dyes from PET that has been depolymerized

Figure 3 – Shows the separation of dyes from multiple colored PET flakes.

Figure 4-a - Depolymerized Nylon 6,6 carpet

Figure 4-b - Depolymerized nylon 6 from carpet yarn

Conclusion

The CTH chemical process described above has been under development and evaluation for 4 years. Tires and biomass are converted into a carbonaceous product containing 84 % and higher carbon contents at lower temperature, within 30-90 minutes and without loss of carbon as carbon oxides. In addition to producing carbon, CTH can be employed to liquefy and devulcanize rubber for potential reuse applications under described conditions.

As shown, polymers are effectively depolymerized or polymers separate from copolymers, color, and foreign materials. Complete or partial DP of polymers from copolymers, carbon fibers, glass fibers, and metals are rapidly achieved under milder and more controllable conditions than processes cited in the literature. Recycling of waste materials is required to reduce the environmental problems associated with their disposal. The four years of study strongly indicates that this developing process offers an energy savings, non-polluting, cost-effective means to transform waste into a number of useful products. Commercialization of application of this technology is planned to be initiated in 2012. We will be happy to provide additional information upon request.

Submitted by BCD Group-II, Inc.

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